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SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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Novel polymer surfactants based on the branched silatrane-containing polyesters and polyethers

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Objectives. *Biologically active polymeric surfactants are a new promising class of macromolecules that can find application in medicine, cosmetology, and agriculture. In this study, a number of new biologically active amphiphilic polymers based on branched silatrane-containing polyesters and polyethers were obtained, and their surface-active properties were investigated.*

Methods. *The branched polymers were represented by polyethers and polyesters, obtained respectively via the anionic polymerization of 1,2-epoxypropanol or a combination of equilibrium polycondensation and ring opening polymerization. The polymers were modified with 3-isocyanopropylsilatrane and trimethylethoxysilane to obtain the amphiphilic compounds containing silatrane groups bonded to the polymer backbone by the urethane bond. The structure of the synthesized polymer silatranes was confirmed via nuclear magnetic resonance spectroscopy and gel permeation chromatography. The surface active properties of all the copolymers obtained were investigated in connection with their obvious amphiphilicity. In particular, the formation of micelles in aqueous solutions is such a property. The critical micelle concentrations were determined by a method of quenching the fluorescence of the polymers.*

Results. *It was shown that the values of the critical micelle concentrations and the hydrophilic-lipophilic balance values of polymers determined by the Griffin equation correlate well with each other. A linear relationship between the hydrophilic-lipophilic balance and the critical micelle concentrations was established. At the same time, polyether-based polymers generally showed higher critical micelle concentrations than polyester-based polymers, although the hydrophilic-lipophilic balance values for polymers of different series, but with close degrees of substitution, were close. It was found that the use of all synthesized polymers as stabilizers of direct and reverse emulsions leads to an increase in the aggregative stability of both types of emulsions. The stability of emulsions depended both on the degree of substitution of peripheral hydroxyl groups of polymers by silatranes and on the molecular weight and structure of the branched block of polymers. The stability of direct emulsions increased for all polymers, while that of inverse emulsions decreased with an increasing degree of substitution of hydroxyl groups by silatranes. The increase of the branched block molecular weight led to an increase of droplet sizes for both direct and inverse emulsions. The smallest droplet size for direct and inverse emulsions was obtained using polymers with low molecular weight branched polyester blocks as surfactants.*

Conclusions. *The results obtained prove the possibility of creating polymer surfactants containing silatrane groups. By varying the structure of the polymer, its molecular weight and the degree of substitution of peripheral functional groups, it is possible to obtain surfactants with desired surface properties.*

Keywords: *branched polymers, silatranes, micellization, emulsions.*

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Новые полимерные ПАВ на основе разветвленных силатрансодержащих полиэфиров

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Цели. *Биологически активные полимерные ПАВ являются новым многообещающим классом макромолекул, которые могут найти применение в медицине, косметологии, сельском хозяйстве. В данном исследовании был получен ряд новых амфифильных полимеров на основе разветвленных силатран-содержащих полиэфиров и исследованы их поверхностно-активные свойства.*

Методы. *Разветвленные полимеры были представлены простыми и сложными полиэфирами, которые получали соответственно способом анионной полимеризации 1,2-эпоксипропанола либо комбинацией равновесной поликонденсации и полимеризации с раскрытием цикла. Для получения амфифильных соединений, содержащих силатрановые группы, связанные с полимерным каркасом уретановой связью, полимеры были модифицированы 3-изоцианопропилсилатраном и триметилэтоксисиланом. Структура синтезированных полимерных силатранов была подтверждена методами ЯМР-спектроскопии и гель-проникающей хроматографии. Поверхностно-активные свойства всех полученных сополимеров были исследованы в связи с их очевидной амфифильностью, в частности, таким свойством является образование мицелл в водных растворах. Методом гашения флуоресценции полимеров были определены величины критических концентраций мицеллообразования (ККМ).*

Результаты. *Показано, что величины ККМ и определенные в соответствие с уравнением Гриффина величины гидрофильно-липофильного баланса (ГЛБ) для полимеров коррелируют, при этом была установлена линейная зависимость между указанными величинами. Полимеры на основе простых полиэфиров в целом показывали более высокие значения ККМ, чем полимеры на основе сложных полиэфиров, хотя величины ГЛБ для полимеров разных серий, но с близкими степенями замещения были близки. Было обнаружено, что использование всех синтезированных полимеров в качестве стабилизаторов прямых и обратных эмульсий приводит к увеличению агрегативной устойчивости эмульсий обоих типов. Устойчивость эмульсий зависела как от степени замещения периферийных гидроксильных групп полимеров силатранами, так и от молекулярной массы и строения разветвленного блока полимеров. Для всех полимеров устойчивость прямых эмульсий возрастала, а обратных эмульсий – снижалась с увеличением степени замещения гидроксильных групп силатранами. С увеличением молекулярной массы разветвленного блока размеры капель как прямых, так и обратных эмульсий увеличивались. Наименьший размер капель прямой и обратной эмульсии был получен при использовании в качестве ПАВ полимеров с низкомолекулярными разветвленными блоками на основе сложных эфиров.*

Заключение. *Полученные результаты показывают возможность создания полимерных ПАВ, содержащих силатрановые группы. Варьируя строение полимера, его молекулярную массу и степень замещения периферийных функциональных групп, возможно получение ПАВ с заданными поверхностными свойствами.*

Ключевые слова: *разветвленные полимеры, силатраны, мицеллообразование, эмульсии.*

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Introduction

Today, surface active substances (surfactants) are widely used in the food, cosmetic, perfume, and pharmacological industries. Moreover, for biomedical polymer surfactants, properties such as biocompatibility and the ability to decompose into non-toxic and easily released compounds are highly desirable [1]. Polymers, which are surface active substances, in the synthesis of which hydroxy acids – lactic, glycolic, etc. were used as reagents, are the most interesting from the point of view of environmental safety, since when they decompose, substances are formed that are products of the metabolism of living organisms [2, 3]. The attention of many scientists has been attracted not only by the preparation of biocompatible surfactants, but also by the synthesis and study of biologically active surfactants [4]. Such compounds can be the components of dosage forms combining high physiological activity and pronounced transport properties. A number of industrially important surfactants containing heterocyclic fragments and exhibiting bactericidal and antimicrobial activity can serve as an example [8–13]. In addition to the medical industry, the main consumer of biologically active surfactants, these compounds may be used in veterinary medicine and agriculture.

Silatranes are intra-organosilicon esters; their study was started by academician M.G. Voronkov in the 1960s [14]. Due to silatranes' unique antifungal, antibacterial, anti-inflammatory, antiviral and antitumor activity, as well as their pronounced activity in the regulation of plant growth [14–18], these compounds are used in medicine, cosmetology, and agriculture. For example, chloromethylsilatran is known as a highly effective, practically non-toxic, and easily biodegradable stimulator of crop growth and productivity [18–20].

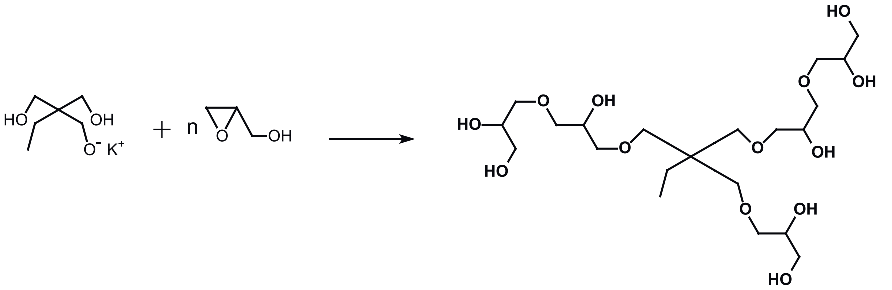
However, in the vast majority of studies, the structure, physicochemical properties, and biological activity of low molecular weight silatranes were studied. To date, there are practically no publications on the biological activity of polymers containing silatrane fragments, while the study of polymeric substances including silatrane groups is of great interest from the point of view of obtaining new bioactive and surface active polymers, as well as expanding the range of available pharmacological agents. To solve this problem, we synthesized a number of amphiphilic branched polymers containing polar lateral silatrane fragments, and evaluated their surface activity.

Materials and Methods

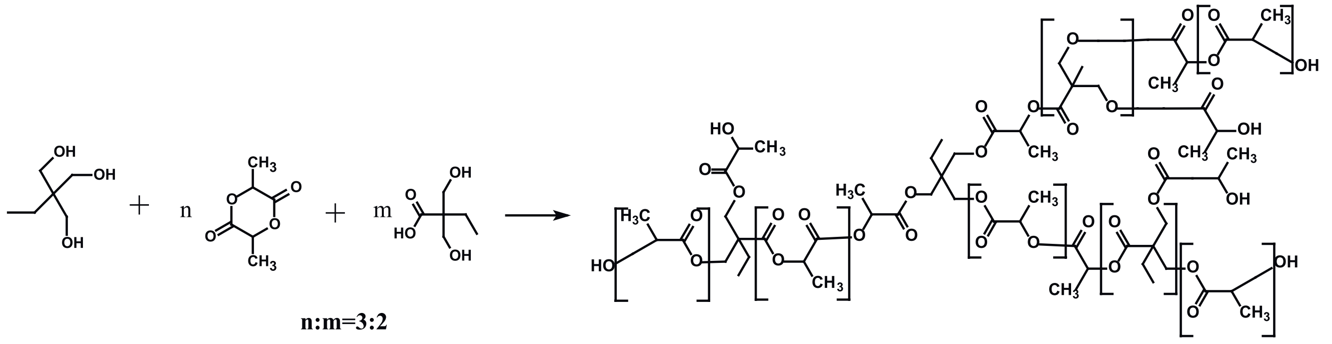
We used 3-isocyanopropyltriethoxysilane (98%), potassium *tert*-butanolate (97%) (*abcr GmbH*, Germany), triethanolamine ("pure"), diglyme ("pure") (*Khimmed*, Russia), 1,2-epoxypropanol (96%, *Sigma-Aldrich*, USA), 1.1.1-tris(hydroxymethyl)propane (97%), tin(II) 2-ethylhexanoate (Sn(Oct)2) (97%), trimethylethoxysilane (97%) (*Acros Organics*, USA), 2.2-bis(hydroxymethyl)butanoic acid (98%, Acros Organics, USA), diethyltin dicaprylate (DEDCO, 98%, *Abika*, Russia) without additional processing. Tetrahydrofuran (THF), benzene, methylene chloride (*Khimmed*, Russia), L-lactide (98%, *Sigma-Aldrich*, USA) were purified by standard methods [21].

As objects of study, biocompatible branched polymers were obtained that have different structures and molecular weights. These polymers were either polyethers (Scheme 1) or polyesters (Scheme 2), most of whose functional groups were on the peripheral part of the macromolecule. The synthesis was carried out, respectively, by the method of anionic polymerization of 1,2-epoxypropanol according to the aforementioned method [22] (Scheme 1), or by a combination of equilibrium polycondensation and polymerization with ring opening according to the procedure [23] (Scheme 2).

The synthesis of low molecular weight silatrane was carried out by modifying the method described in [24] (Scheme 3): a solution of 3-isocyanopropyltriethoxysilane (27.3 g, 0.11 mol) was added to a mixture of triethanolamine (15.0 ml, 16.8 g, 0.11 mol) in benzene (20 ml) and a catalytic amount (5 mg) of potassium *tert*-butanolate. The resulting mixture was heated to 80 °C and silatrane was synthesized for 10 hours by distillation of an azeotropic mixture of benzene and ethanol, at the same time adding to the reaction mixture an equivalent distilled-off amount of dry benzene. After the reaction, the silatrane was left in the form of a 2.2 M solution obtained in the synthesis process, without being isolated as a solid.



Scheme 1



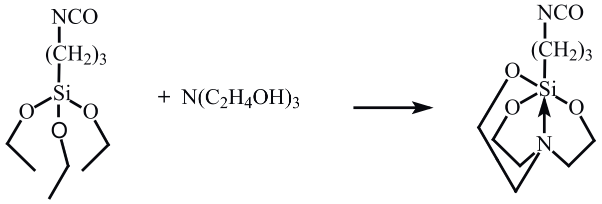
Scheme 2

In the next step, the synthesized polymers were modified with 3-isocyanopropylsilatrane and trimethylethoxysilane (Schemes 4, 5) to obtain amphiphilic compounds.

By varying the ratios of the branched polymer and silatrane used for the synthesis, we obtained polymers with different average degrees of substitution of the hydrophilic groups of branched macromolecules by silatranes. The reactions were carried out in THF with constant stirring and a temperature of 25 °C for 4 hours. In a 50 ml round bottom two-necked flask with a magnetic stirrer, inert gas injection and reflux condenser, the hydroxyl-containing polymer and the calculated amount of DEDCO in 10 ml of THF were dissolved with stirring, after which a solution of 3-isocyanopropylsilatran in THF was added. The synthesis was carried out for 60 min at 66 °C, after which a solution of trimethylethoxysilane excess was added and boiled for another 60 min. After completion of the reaction, the solvent was removed and the polymer was purified via dialysis (THF solvent, “ZelluTrans” dialysis membrane, MVCO 1000 Da) for 24 hours.

The nuclear magnetic resonance (NMR) spectra were recorded for 10% copolymer solutions in $CDCl_3$ on a Brucker spectrometer with an operating frequency of ^1H – 600.22 MHz and ^{13}C – 150.94 MHz (internal standard is tetramethylsilane) at the Center for Molecule Composition Studies of the Institute of Organoelement Compounds of the Russian Academy of Sciences (INEOS RAS).

Gel permeation chromatography (GPC) of the copolymers was carried out on a Waters 150 chromatograph, eluent — was THF, the flow rate was 1 ml/min, with the PL-GEL 5u MIXC column (300 × 7.5 mm), at the Center for Molecule Composition Studies of the INEOS RAS.

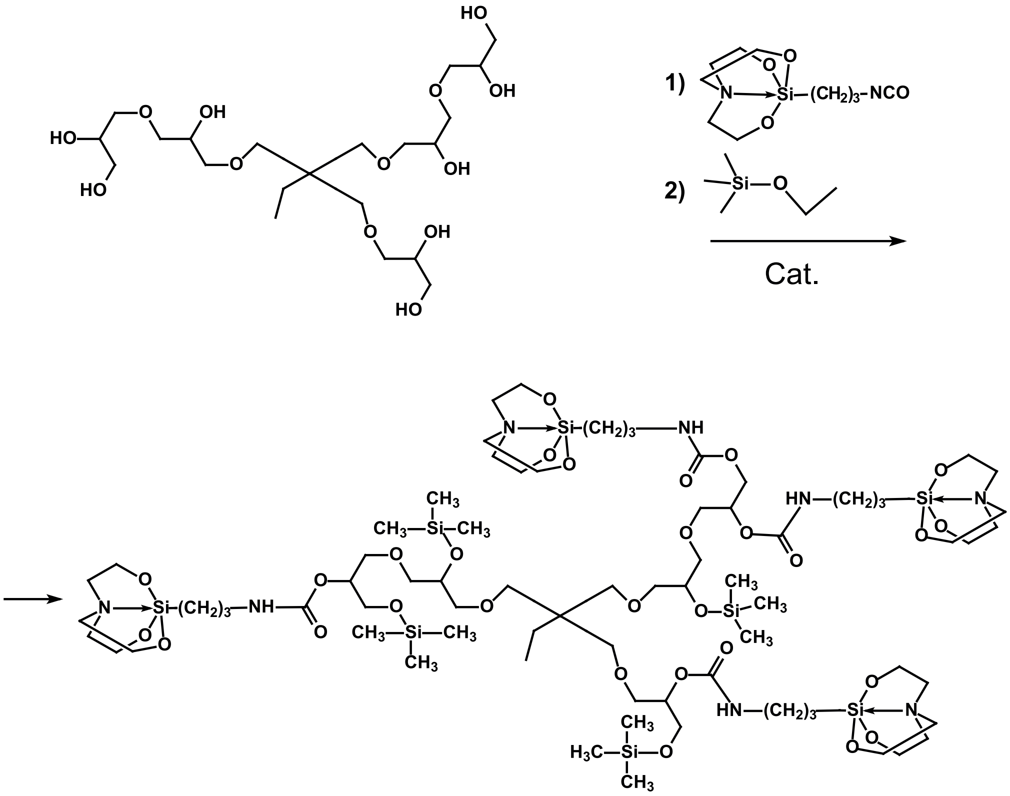


Scheme 3

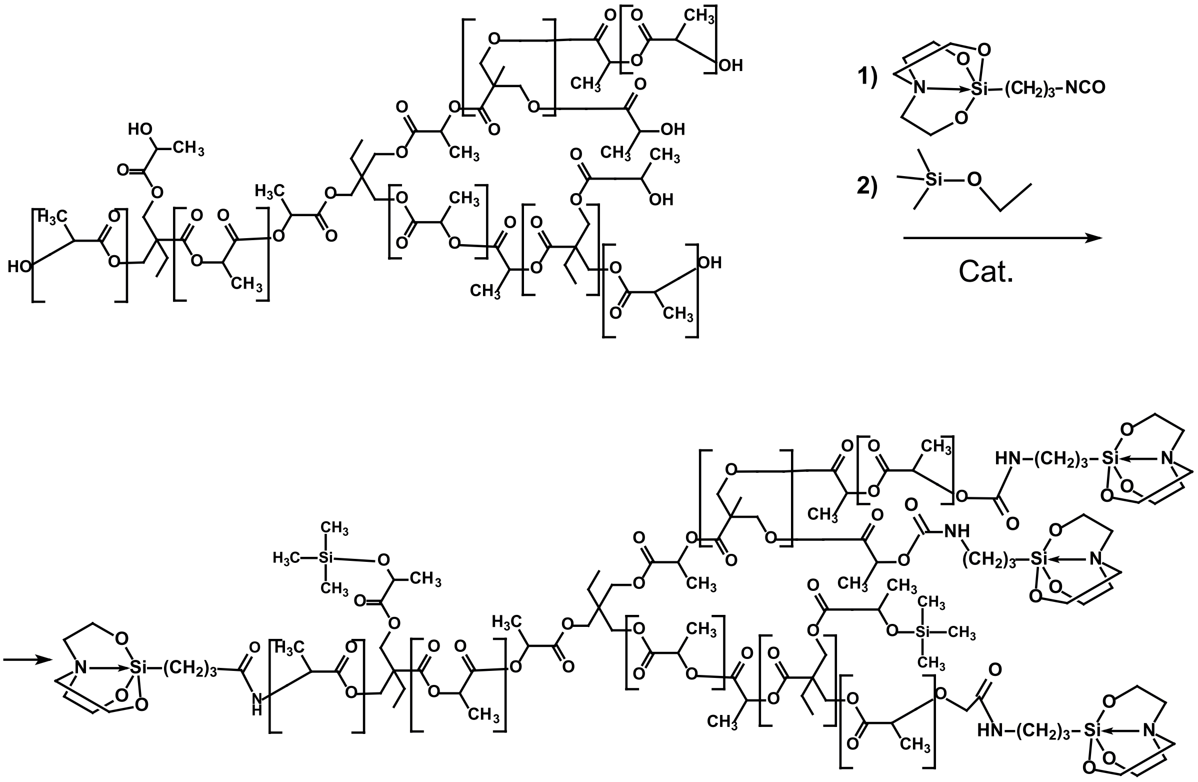
The value of the hydrophilic-lipophilic balance (HLB) for the polymer was determined according to Griffin [25]. The analytical expression of HLB for surfactant molecules is HLB = $20(M_h/M)$, where M_h and M are the molecular weights of the hydrophobic fragment and the whole molecule. For all the polymers studied, the branched macromolecular backbone was considered as hydrophobic.

The determination of critical micelle concentration (CMC) was carried out via a method of increasing the fluorescence in accordance with the procedure [26], using diphenylhexatriene as a fluorescent label. The fluorescence spectra were obtained at an excitation wavelength of 366 nm and a recording wavelength of 430 nm.

Direct emulsions were obtained by dispersing 4 ml of a 5% copolymer solution in methylene chloride in 40 ml of water (ultrasonic disperser UZDN-A, 30 s, 15 W). The concentration in water of all the copolymers for the resulting emulsions exceeded CMC two-fold. Reverse emulsions were also obtained by ultrasonic treatment, while 0.1 ml of water was dispersed in 10 ml of a 5% copolymer solution (ultrasonic disperser UZDN-A, 30 s, 15 W).



Scheme 4



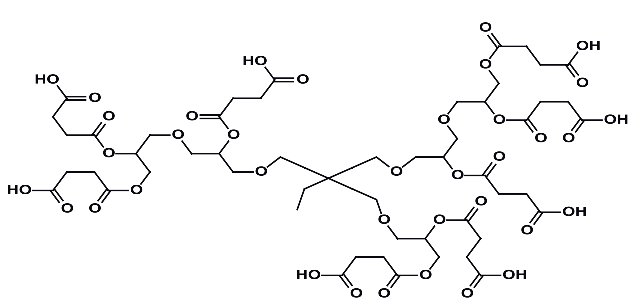
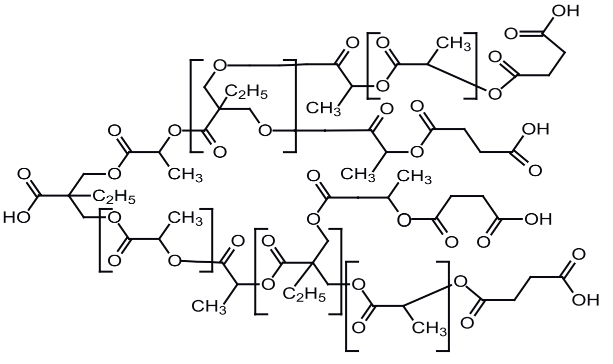
Scheme 5

To determine the average droplet size of the emulsion, we used a Photocor-FC correlation spectrophotometer (*Photocor Instruments Inc.*, USA) with a He-Ne laser radiation source (Coherent, USA, Model 31-2082, 632.8 nm, 10 mW).

Results and Discussion

The branched polymers **I–IV** were obtained in the form of yellowish solids, readily soluble in THF and chloroform. The ^{1}H-NMR spectra of polyethers **I** and **II** contain signals of the macromolecule branched core protons for $–CH_2–CH_3$ (0.88 ppm) and $–CH_2–CH_3$ (1.37 ppm), characteristic of polyglycerol groups, as well as a wide multiplet peak typical for signals of the $–CH_2–O–$ and $–CH<$ groups (at 3.00–4.20 ppm). The ^{1}H-NMR spectra of polyesters III, IV contain signals of proton groups $–CH<$ and $–CH_3$ polylactide units at 5.04 and 1.45 ppm, respectively, as well as signals characteristic of the protons for the $–CH_2$ and $–CH_3$ groups of 2,2-bis-(hydroxymethyl)butanoic acid (1.23 and 0.90 ppm, respectively). Since the signals of the characteristic groups did not overlap in the spectra of all polymers and it was possible to integrate them, the ratio of the corresponding groups in the polymer, the monomer composition, and the molecular weight of the studied macromolecules were determined based on integrated signal intensities characteristic for various comonomers. As can be seen in Table 1, all branched polymers were obtained in high yield, which implies the completeness of the synthesis reaction.

Table 1. Characteristics of synthesized branched polymers

No.	Structure of branched polymer	Yield,%	M_n of copolymer, g/mol		M_w/M_n**
			M_n^{NMR*}	M_n^{GPC} **	
I		99	2300	2350	1.4
II		98	4800	4950	1.5
III		98	2000	2200	1.9
IV		96	5200	5800	2.3

*Determined from the NMR data;
**Determined from the GPC data.

As a result of the reaction of isocyanatopropylsilatrane with branched polymers, two series of amphiphilic compounds with a different structure and composition of the main polymer chains, as well as with an amount of side silatrane and trimethylsilyl fragments were obtained. These polymers were white solid materials, the solubility of which in water depended strongly on the content of silatrane fragments. Thus, polymers with an insignificant (about 10%) content of silatrane groups were poorly soluble in water, while polymers with 97–100% substitution of hydroxyl groups with silatrane groups were easily soluble in water. All amphiphilic polymers were characterized by NMR spectroscopy and GPC. The degree of substitution of free hydroxyl groups was characterized using ^{1}H and quantitative ^{13}C NMR spectroscopy (Table 2). The experimentally determined and theoretically calculated amounts of carboxyl groups substituted by silatranes have close values, which confirms the correspondence of the proposed polymer structures to those obtained.

As a result, we obtained polymers with a branched core formed by polyethers (polymers **1–6**) or polyesters (polymers **7–12**) with low (polymers **1–3**, **7–9**) or high (polymers **4–6**, **10–12**) molecular weight. In this case, polymers **1, 4, 7, 10; 2, 5, 8, 11** and **3, 6, 9, 12** differed in the structure and mass of the branched block, while the degree of substitution of the hydrophilic groups of the branched block by silatranes in these series of polymers were similar.

Table 2. Characteristics of synthesized polymeric silatranes

Sample No.	Branched polymer	Yield, %	Substitution degree*		M_n**	M_w/M_n**
			Calculated	Measured		
1	**I**	97	30	29	3300	2.3
2		95	60	57	4300	2.4
3		96	100	97	5550	2.3
4	**II**	93	30	28	6950	2.6
5		95	60	57	8900	2.8
6		92	100	93	11550	3.1
7	**III**	94	30	28	2700	2.8
8		96	60	57	3200	2.6
9		96	100	97	3800	2.7
10	**IV**	97	30	29	11100	3.2
11		97	60	58	16500	3.1
12		95	100	94	17400	3.4

*Degree of substitution of polymer hydroxyl groups by the silatrane fragments, determined via monomer ratios (Calculated) and from the NMR data (Measured).

**Values, determined from the GPC data.

In view of the amphiphilicity of the obtained compounds, their ability to form micelles in aqueous solutions and the properties of their surface activity were studied. CMC values were determined by quenching the fluorescence of polymers. The results are presented in Table 3 together with the HLB values determined by the Griffin equation. Based on the data obtained, it may be noted that the hydrophilic-lipophilic balance of the copolymers within each series changed systematically, while the HLB and CMC values of almost all polymers correlate well with each other, showing a linear relationship between HLB and CMC. Moreover, polymers based on polyethers (polymers **1–6**) generally showed higher CMCs than polymers based on polyesters (polymers **7–12**); although the HLB values for polymers of different series but with similar degrees of substitution were close.

Table 3. Surface-active properties of polymeric silatranes

Polymer	HLB	CMC, mol/L	Polymer	HLB	CMC, mol/L
1	6.1	2.2×10^{-5}	**7**	3.7	1.2×10^{-6}
2	9.3	3.2×10^{-3}	**8**	6.3	8.1×10^{-4}
3	11.7	5.8×10^{-1}	**9**	8.4	2.6×10^{-1}
4	6.2	3.1×10^{-4}	**10**	9.5	9.6×10^{-7}
5	9.2	6.3×10^{-3}	**11**	13.0	8.7×10^{-3}
6	11.7	7.1×10^{-1}	**12**	13.3	1.4×10^{-2}

Since one of the possible applications for synthesized copolymers is their use as surfactants during micro- and nanocapsulation, the study of the aggregative stability of emulsions stabilized by such compounds is of great importance. In connection with this, we evaluated the stability of direct and reverse emulsions stabilized by polymers **1–12** (Table 4).

It was found that all the copolymers studied were able to increase the aggregative stability of inverse emulsions: the size of inverse emulsion droplets in the presence of polymers **1–12** increased 2.1–6.1 times in 30 minutes, while without the use of polymers the size of the drops of the emulsion increased by 14.5 times. The stability of inverse emulsions depended both on the degree of substitution of peripheral hydroxyl groups of polymers with silatranes and on the molecular weight and structure of the branched block of polymers. The smallest emulsion droplets were obtained when polymers with a low molecular weight polyester branched block were used as surfactants. The size of the droplets of the emulsions increased when increasing the molecular weight of the branched block. A similar dependence in

Table 4. Size of the emulsion droplets, obtained from the solutions of polymeric silatranes

Polymer	Size of the reverse emulsion droplets (nm), after			Size of the direct emulsion droplets (nm), after		
	1 min	10 min	30 min	1 min	10 min	30 min
– *	58	490	840	175	1080	–**
1	57	211	270	179	580	870
2	58	227	285	175	471	552
3	62	254	328	188	338	470
4	54	191	242	184	479	690
5	56	218	280	180	434	537
6	57	270	350	188	371	430
7	56	118	140	200	437	727
8	55	169	210	191	377	464
9	58	199	250	205	350	416
10	56	209	265	212	570	760
11	56	231	297	200	532	687
12	57	247	321	196	422	596

*Emulsions, obtained without surfactants.

**Water release as a separate phase was observed.

the size of the inverse emulsion's droplets on the size of the branched block was also observed in polymers with a branched block based on simple ether (polymers **1–6**). For all the polymers, the stability of reverse emulsions decreased with increasing degree of substitution of hydroxyl groups with silatranes.

All the copolymers studied were able to increase the aggregative stability of direct emulsions as well: the sizes of direct emulsion droplets in the presence of **1–12** polymers increased 2.1–4.6 times in 30 minutes, which is much less than the increase in emulsion droplets without using polymers. The stability of direct emulsions, as well as reverse ones, depended both on the degree of substitution of peripheral hydroxyl groups of polymers with silatranes and on the molecular weight and structure of the branched block of polymers. When polymers with low molecular weight branched polyester blocks were used as surfactants, emulsions with the smallest droplet size were obtained: with increasing the molecular weight of the branched block, the size of the droplets of the emulsions increased. A similar dependence in the size of direct emulsion droplets on the size of a branched block was also observed in the case of polymers with a branched block based on ether (polymers *1–6*); although for these polymers the decrease in the droplet size of the emulsion with an increase in the branched polymer core was less pronounced. For all the polymers, the stability of direct emulsions increased with an increase in the degree of substitution of hydroxyl groups with silatranes.

Thus, the obtained results show the possibility of creating polymer surfactants containing silatrane groups. By varying the structure of the polymer, its molecular weight and the degree of substitution of peripheral functional groups, it is possible to obtain surfactants with the desired surface properties.

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The authors declare no conflict of interest.

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